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Sean M. Ramirez, Yvonne Diaz, Timothy S. Haddad, Joseph M. Mabry

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10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

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THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER

Synthesis and Free Radical Polymerization of Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS) Macromers: Precursors for Low Surface Energy Materials and Devices

Sean M. Ramirez,[1] Yvonne Diaz,[2] Timothy S. Haddad,[1] and Joseph M. Mabry[2]

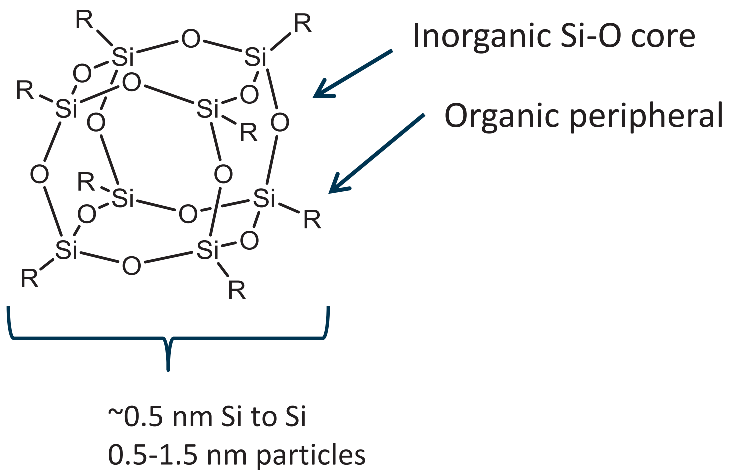
[1]ERC Inc., Air Force Research Laboratory, Edwards AFB, CA 93524-7680 U.S.A.
Phone: (661) 275-5769, sean.ramirez.ctr@edwards.af.mil

[2]Air Force Research Laboratory, Edwards AFB, CA 93524-7680 U.S.A.

FLUOROPOLYMER 2012

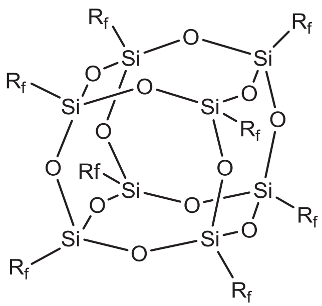
Polyhedral Oligomeric Silsesquioxane POSS $(RSiO_{1.5})_n$

- Organic-inorganic framework
- Well-defined, 3-D nanostructure
- Can carry *functional* groups
- Thermally and chemically robust
- Used in thermoset and thermoplastic polymers, temperature nanocomposites, coatings, surface modifiers, and many other applications



Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, *110, 2081.*
Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Current Opinion in Solid State and Materials Science* **2004**, *8, 21.*

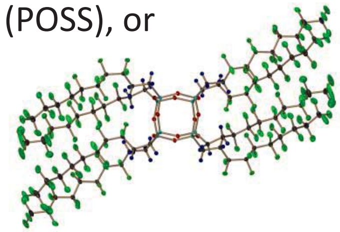
Introduction to F-POSS



$R_f = -(CH_2)_2(CF_2)_7CF_3$

(1,1,2,2-tetrahydroperfluorodecyl)$_8$Si$_8$O$_{12}$ Polyhedral Oligomeric Silsesquioxane (POSS), or fluorodecyl POSS

- hybrid organic-inorganic structure
- well-defined polyhedral architecture
- long-chain fluoroalkyl substituents on periphery of cage

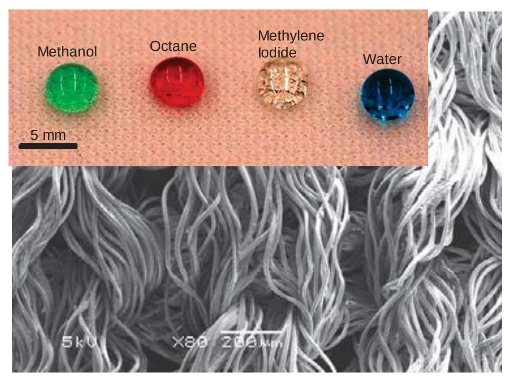


Due to its unique structure, fluorodecyl POSS has one of the lowest surface energies of any crystalline solid currently known

- fluorodecyl POSS	9.3 mN/m
- polytetrafluoroethylene	18-20 mN/m
- CF_3 monolayer	6.7 mN/m

Low surface energy and other unique properties of fluorodecyl POSS has enabled the development of various types of tunable non-wetting polymeric surfaces

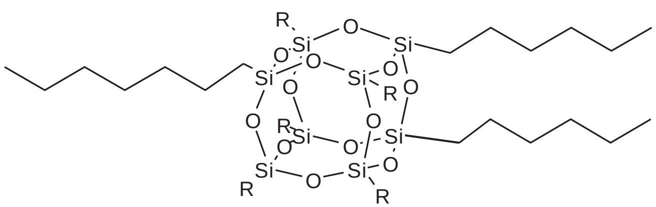
Superhydrophobic/oleophilic dip-coated fabric
Tuteja *et al*, Science, **2007**, 318, 1618



Superamphiphobic dip-coated fabric
Choi *et al*, Adv Mater, **2009**, 21, 2190

Superamphiphobic electrospun surfaces
Tuteja *et al*, PNAS, **2008**, 105, 18200

POSS Incorporation in Polymers



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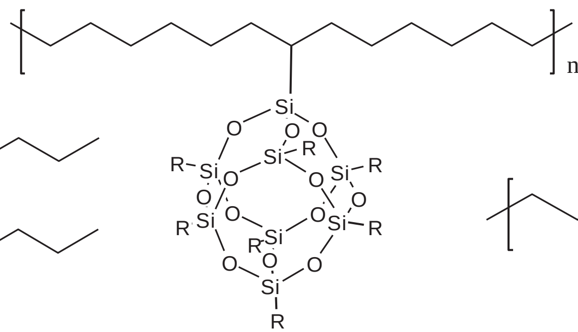
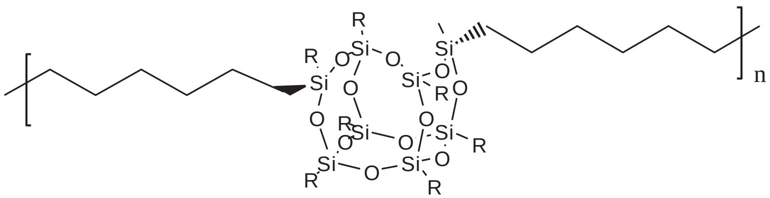
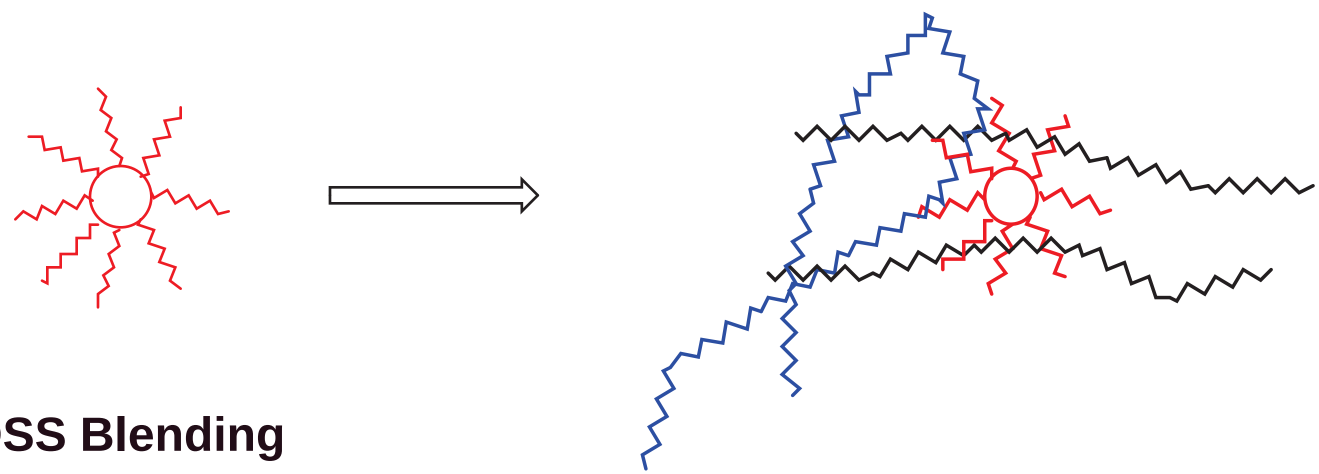


Pendant Polymer



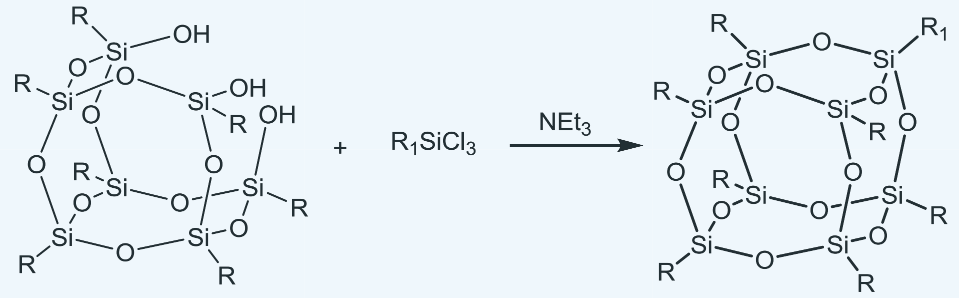
Bead Copolymer



POSS Blending

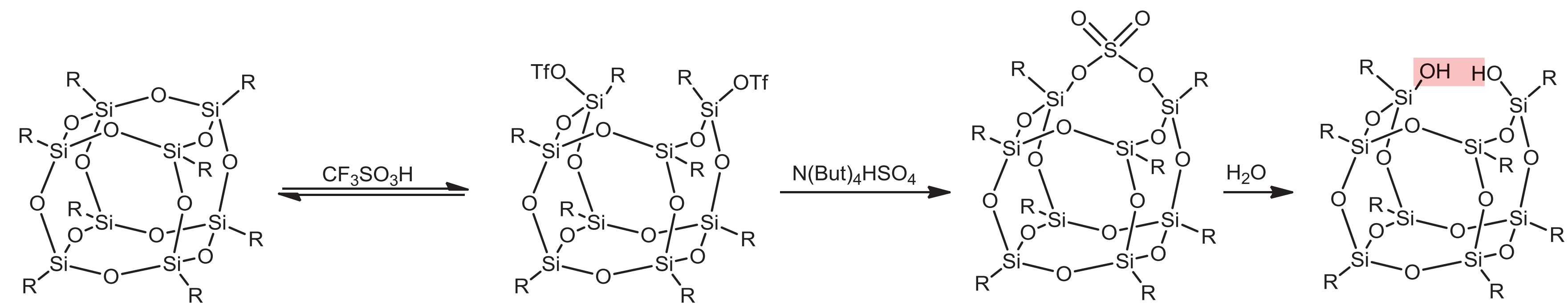
Functional F-POSS (Open-Caged)

- Close-caged structures are accessible and have proven versatile in polymer composites
  - Limitations
    - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
  - Open door for use a *building block* material for *low surface energy materials*
- Applications
  - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
    - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
  - Effects on polymer composite properties
    - Wetting, phase behavior, solubility, etc….



- Open cages lead to functional POSS structures
- Reactions are simple
- High yields typically reported

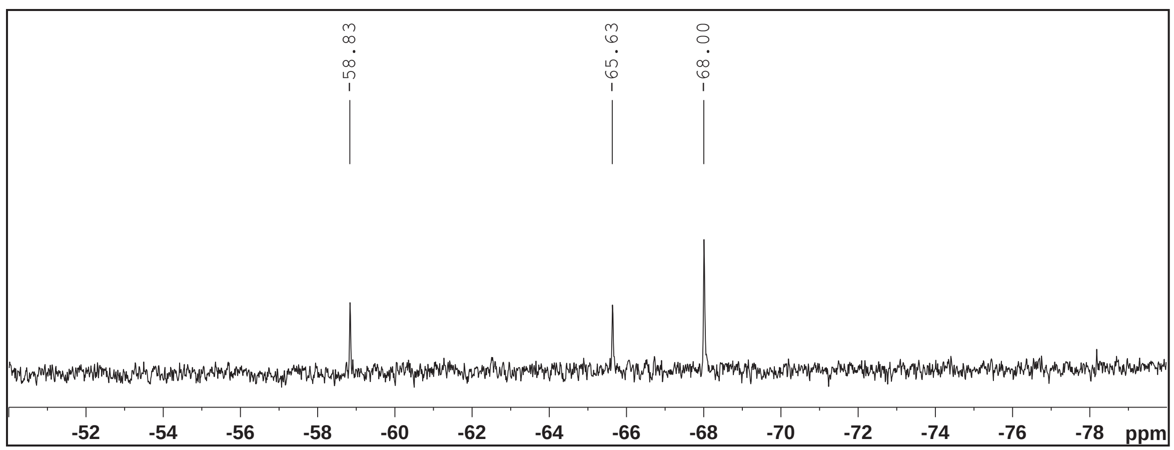
Incompletely Condensed Silsesquioxane



$R_f = CH_2CH_2(CF_2)_7CF_3$

- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.

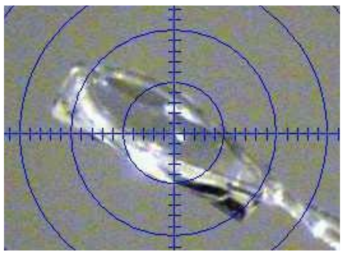
^{29}Si NMR in C_6F_6 of disilanol F-POSS

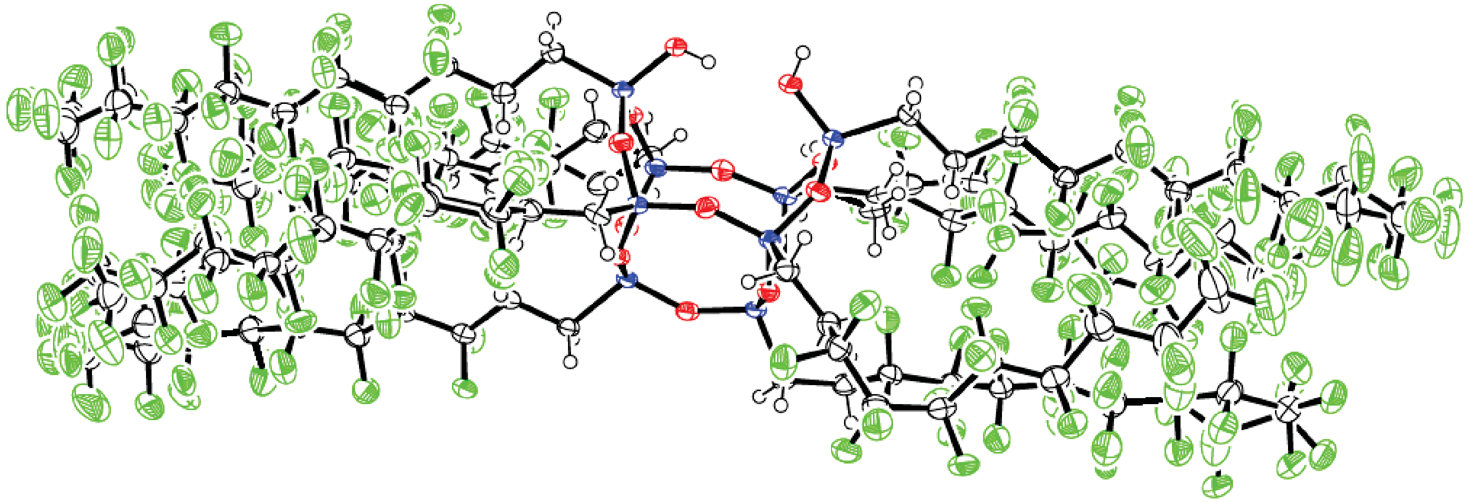


Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Haddad, T. S.; Mabry, J. M. ACS Symposium Series" Advances in Fluorine Containing Polymers 2012 1106, 95-109.

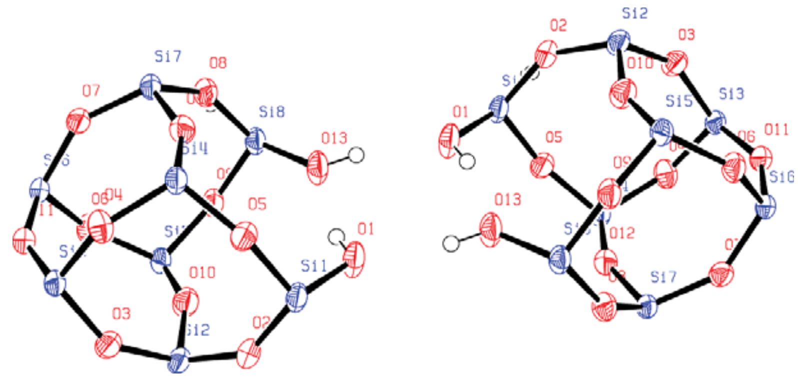
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, **2011**, *133*, 20084.

X-Ray Crystal Structure of Disilanol





- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- M_r=,monoclinic, space group P2(1)/c , a=11.84(10) Å, b=57.11(6) Å, c=19.06(2) Å, α= 90.00°, β=92.21(10) °, γ=90.00 °, V= 12878(2) Å^3



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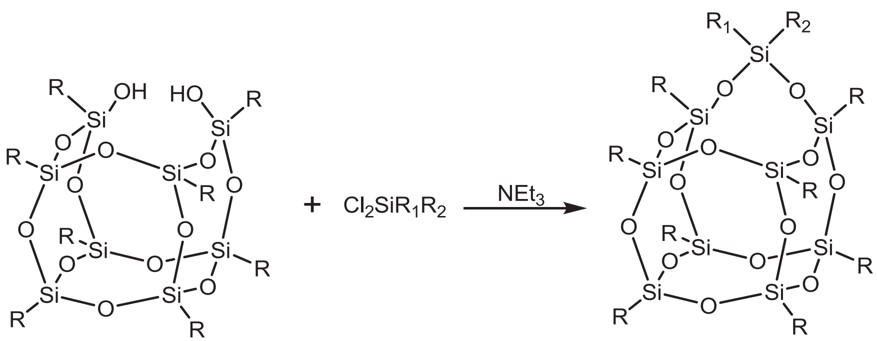
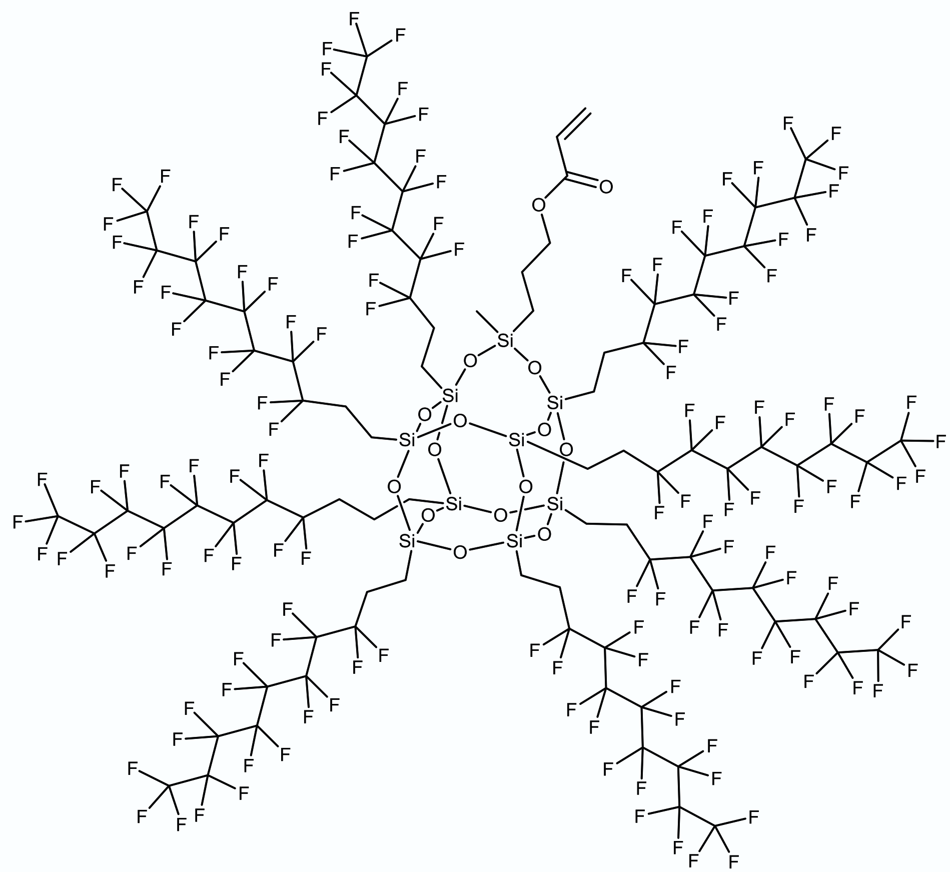
Edge Capping Reactions



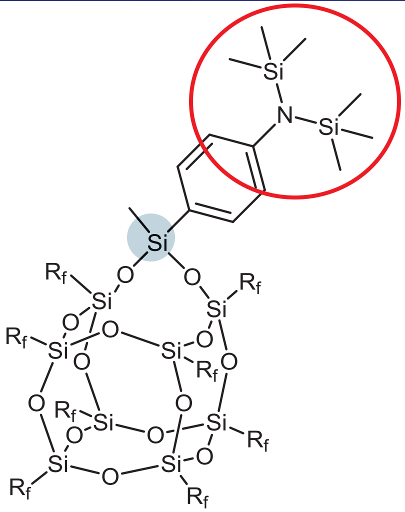
R = $CH_2CH_2(CF_2)_7CF_3$
R_1 = alkyl or aromatic
R_2 = alkyl or aromatic

- Edge capping reactions typically have 40-90% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction

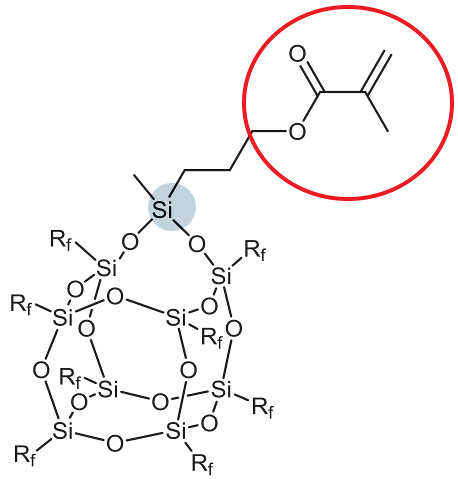


Macromer/RBM = 4178 g/mol

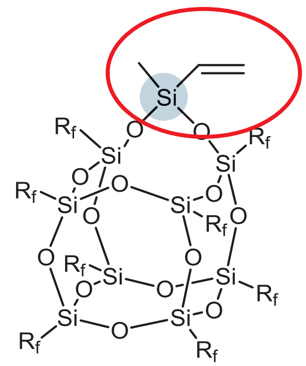
F-POSS Structures Synthesized



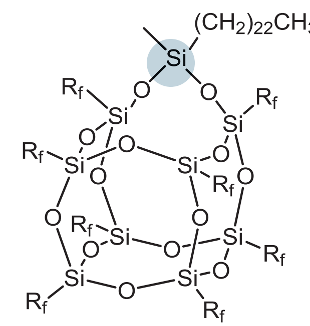
-29.5 ppm



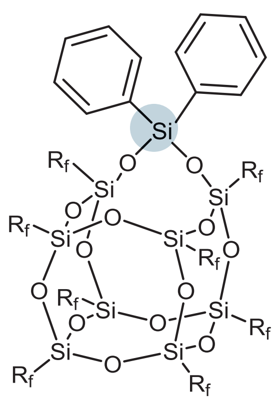
-17.8ppm



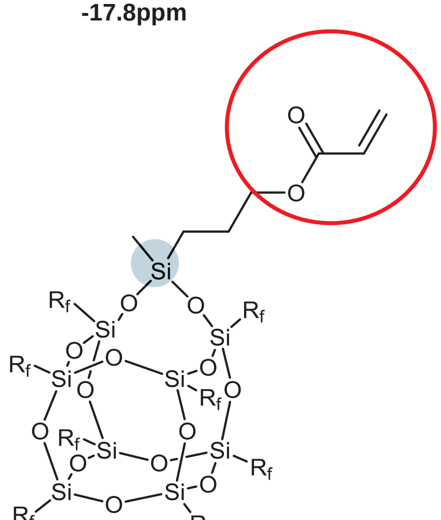
-32.1 ppm



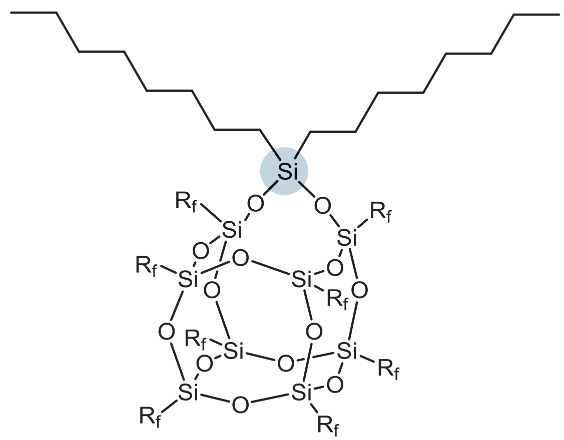
-17.8 ppm



-45.5 ppm



-17.1 ppm

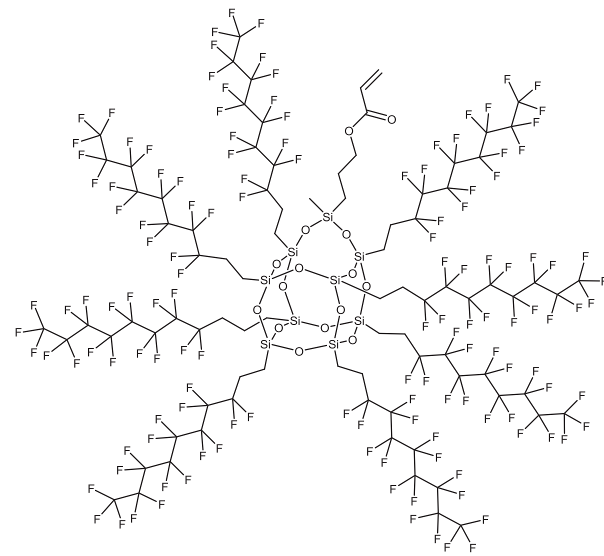


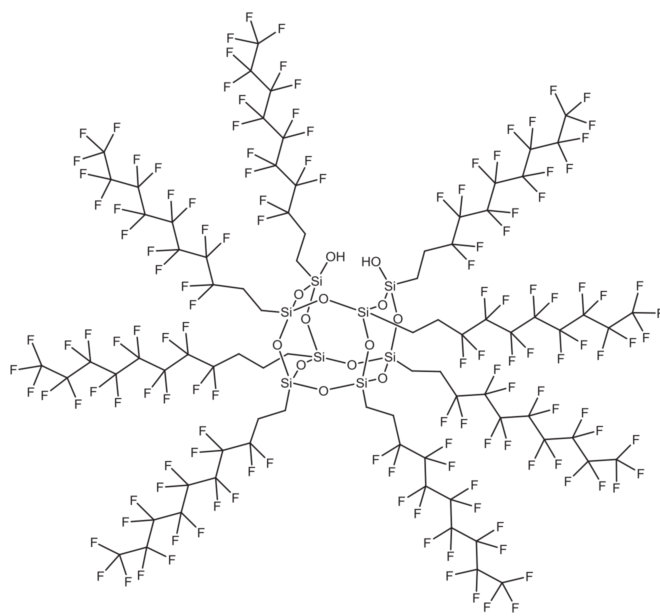
-17.9 ppm

R = $CH_2CH_2(CF_2)_7CF_3$

Contact Angle Measurements

- Non-wetting surfaces can be developed by a combination of three parameters
  - Chemical functionality (high fluorine content)
  - Roughness (micro- and nanoscale)
  - Surface Geometry (re-entrant curvature)
- *What type of influence will functional groups have on F-POSS surface properties?*
- *Solvent impact?*





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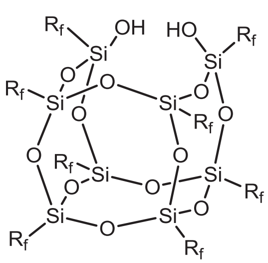
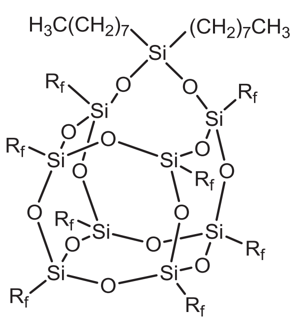
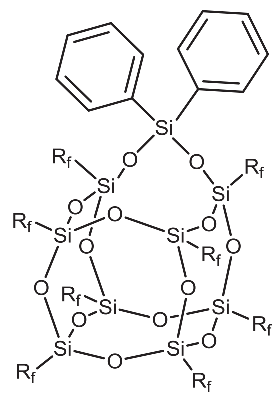
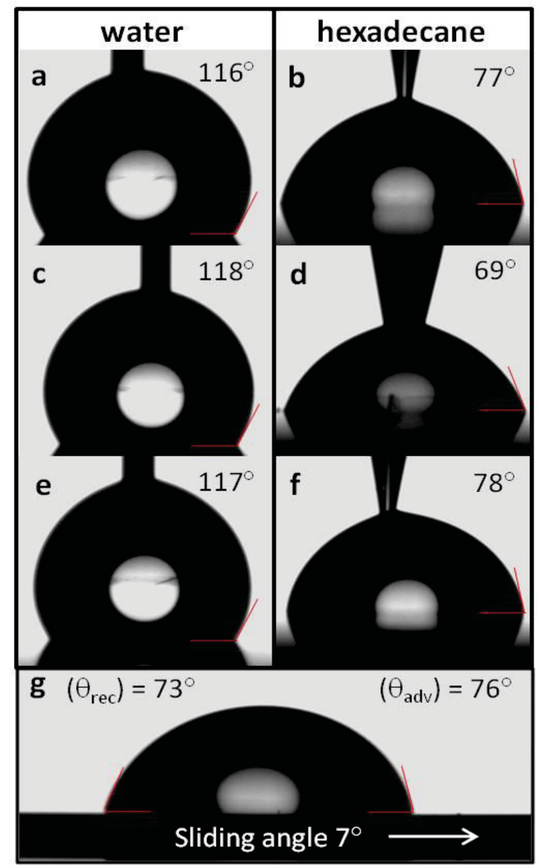


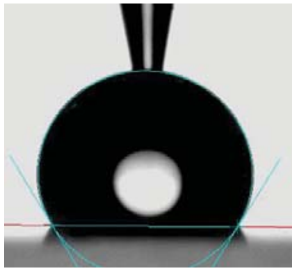






Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10μL) rolling off surface coated with compound **diphenyl** (g).

Dynamic Contact Angle Measurements



Functional Group on F-POSS	water		hexadecane	
	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
F-POSS*	124 ± 0.5°	109.6 ± 0.7°	79.1 ± 0.4°	65.1 ± 0.5°
Si-$(OH)_2$	116.8 ± 0.4°	111 ± 0.6°	77.4 ± 0.4°	74.4 ± 0.8°
Si-$(CH_3)(CH{=}CH_2)$	116.2 ± 0.4°	100.6 ± 0.8°	78.4 ± 0.3°	70.6 ± 2.3°
Si$((CH_3)((CH_2)_3OC(O)CCH{=}CH_2)$	118.2 ± 1.0°	90.6 ± 1.0°	76.8 ± 0.3°	64.8 ± 1.0°
Si-$(CH_3)((CH_2)_3OC(O)C(CH_3){=}CH_2)$	117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°
Si-$(CH_3)((CH_2)_{22}CH_3)$	117.9 ± 0.4°	96.9 ± 1.9°	78.0 ± 0.4°	16.2 ± 5.5°
Si-$(C_6H_5)_2$	116.2 ± 0.4°	110.5 ± 0.5°	76.0 ± 0.8°	73.2 ± 0.4°
Si-$((CH_2)_7CH_3)_2$	117.9 ± 0.5°	95.5 ± 0.4°	69.1 ± 1.2°	23.1 ± 1.2°

Samples (10 mg/mL) were spin casted on oxygen-plasma cleaned Si wafers at 900 rpm for 30 seconds. Contact angle measurements were run in triplicate. Surface roughness < 5nm (AFM and Optical Profilometry).

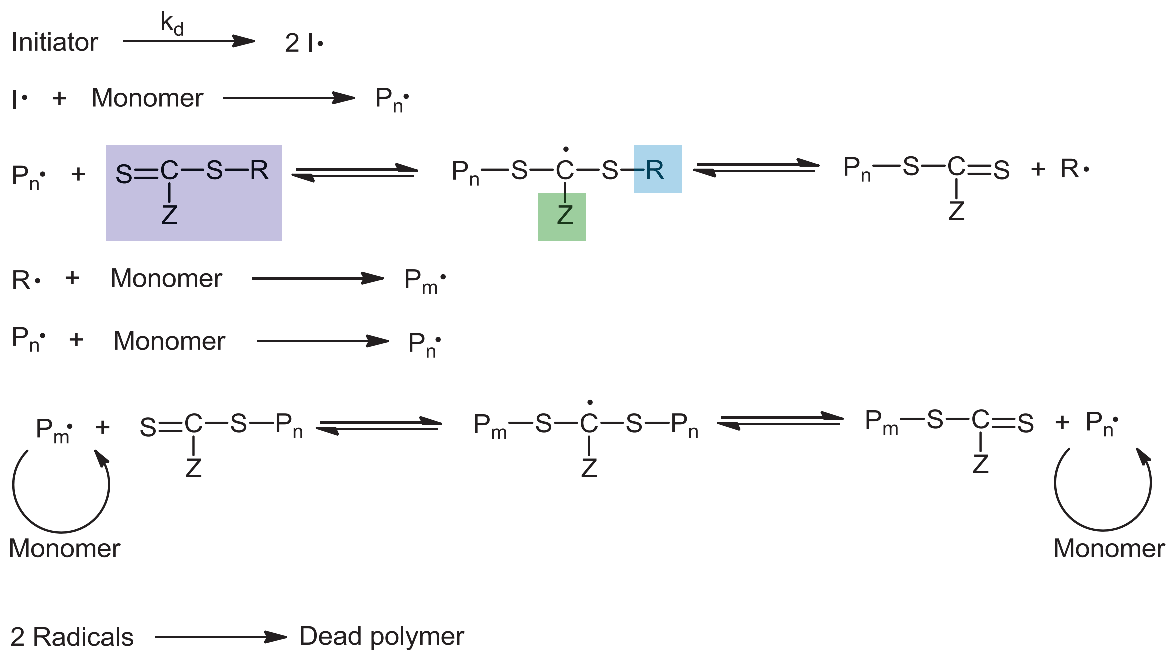
*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3544.

Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization

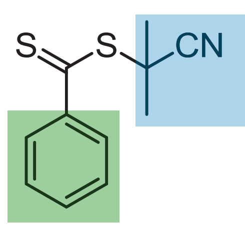
Initiation

Propogation

Termination



Chain Transfer Agent

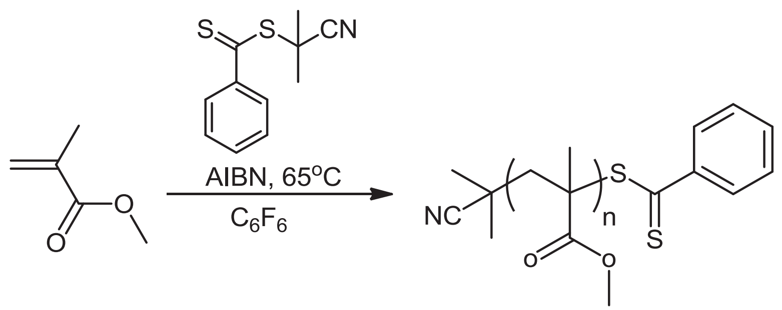


RAFT Polymerization

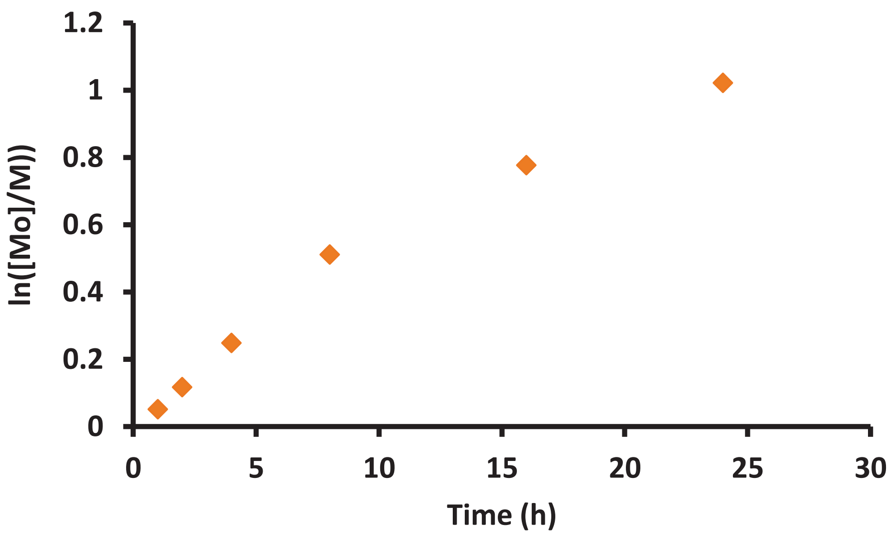
- Controlled polymerization
- Allows for block copolymers
- Tune molecular weight

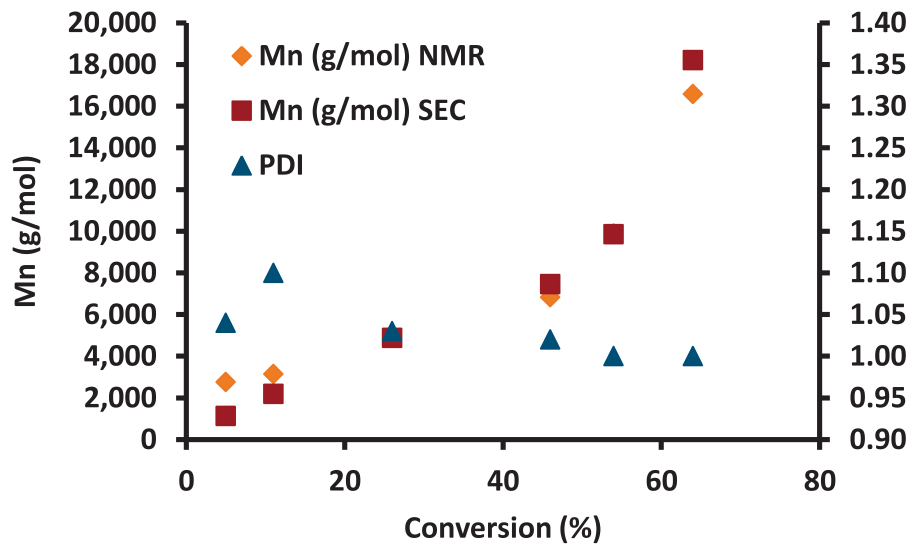
Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living Free Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules* 1998, *31*, 5559−5562

RAFT polymerization of MMA in C_6F_6



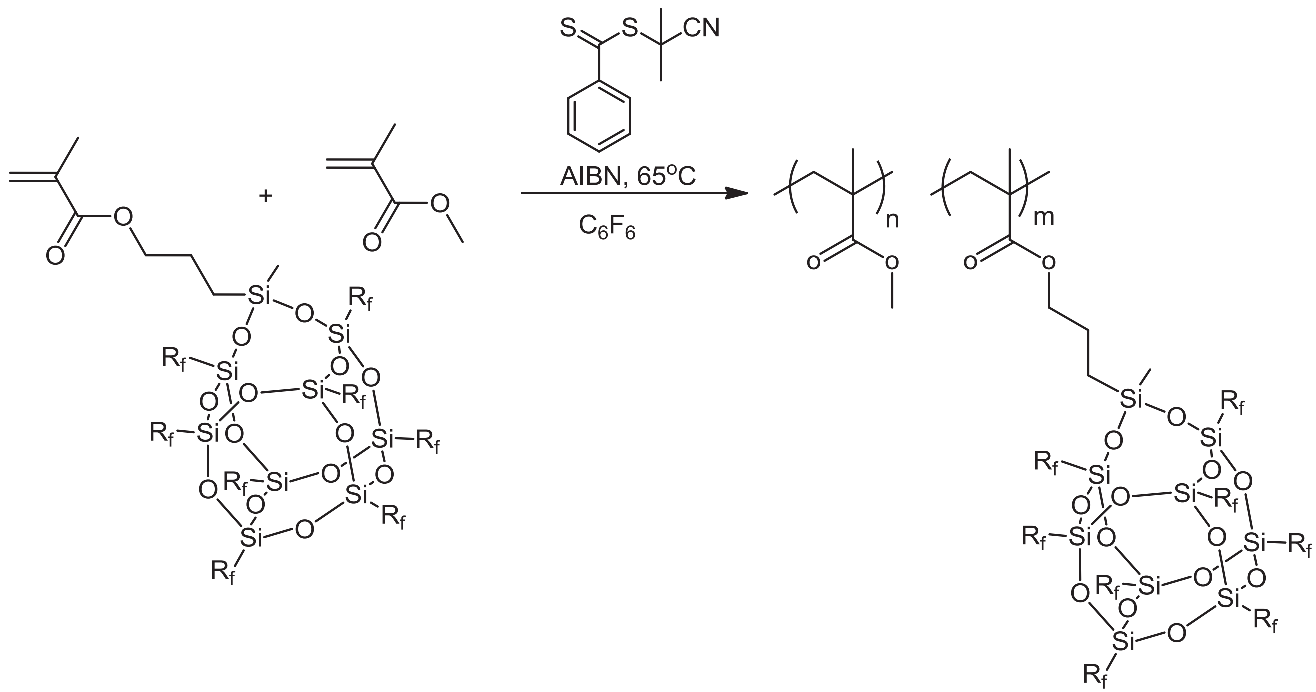
- Testing RAFT in fluorinated solvent
- RAFT polymerization proceeds in C_6F_6
- Best control in first 10 hours





SEC MALS: RI and LS detector (Wyatt), 1.0 mL/min, 30 min, THF.

RAFT copolymerization of P(F-POSS-MA)-co-PMMA



RAFT polymerizations are performed in fluorinated solvent following methods developed for MMA.

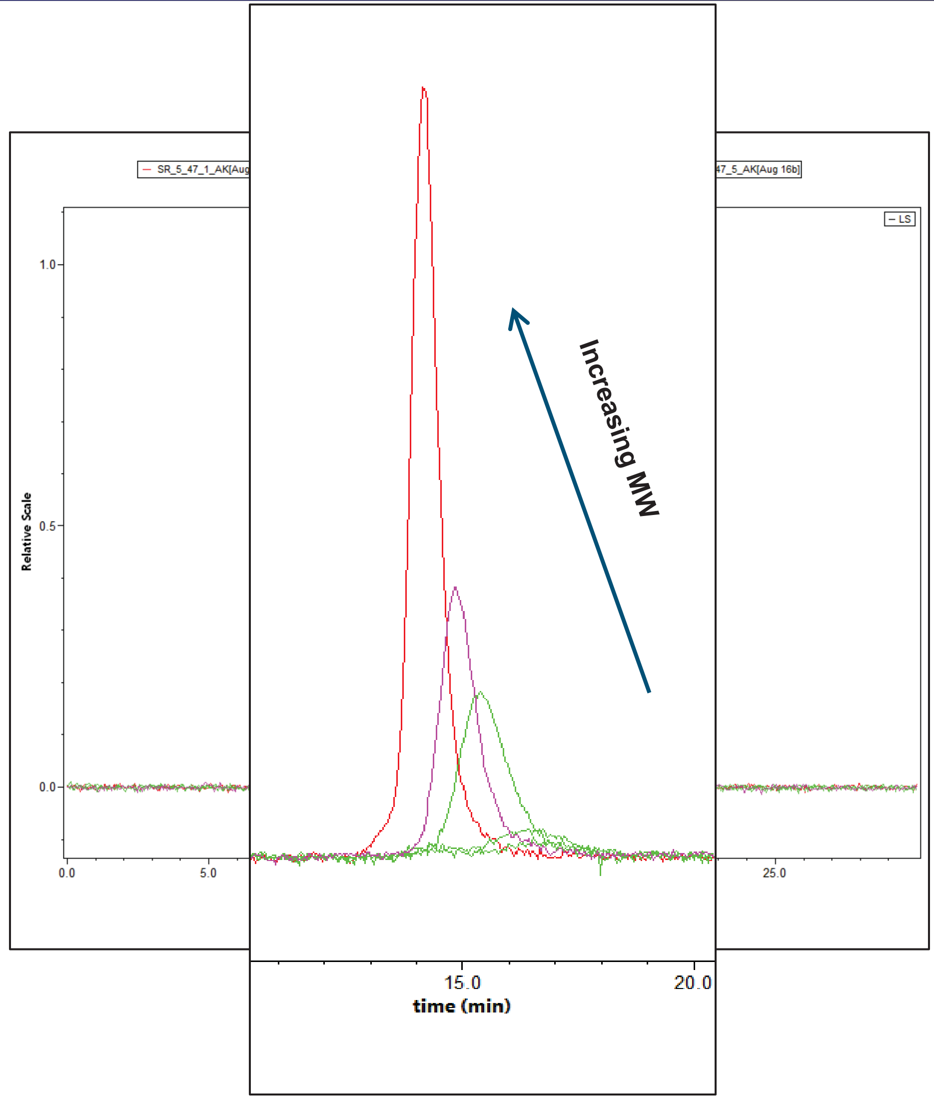
RAFT copolymerization of P(F-POSS-MA)-co-PMMA

F-POSS	M_n		Conv	water		hexadecane	
wt %	(g/mol)	PDI	%.	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
	F-POSS-MMA			117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°
0	45,000	1.05	80	77.8 ± 1.3°	57.8 ± 2.5°	wetted	wetted
1	53,700	1.08	72	109.2 ± 2.4°	61.5 ± 1.9°	67.8° ± 1.4	wetted
5	22,900	1.01	30	117.8 ±1.6°	95.7 ± 5.9°	76.7 ± 1.1°	68.8 ± 1.9°
10	26,600	1.01	29	118.2 ± 1.4°	101.1 ±2.5°	77.2 ± 0.4°	69.5 ± 2.1°
25	36,600	1.03	41	120.8 ± 97.0°	97.0 ± 2.4°	82.9 ± 0.4°	74.6 ± 2.0°

SEC-MALS conditions: 25°C, flow rate (1 mL/min), solvent (Asahiklin-225), concentration measured with RI detector. Contact angle conditions: polymer solutions (20 mg/mL) were spun cast on SiO_2 wafers at 900 rpm with a 30 second dwell time.

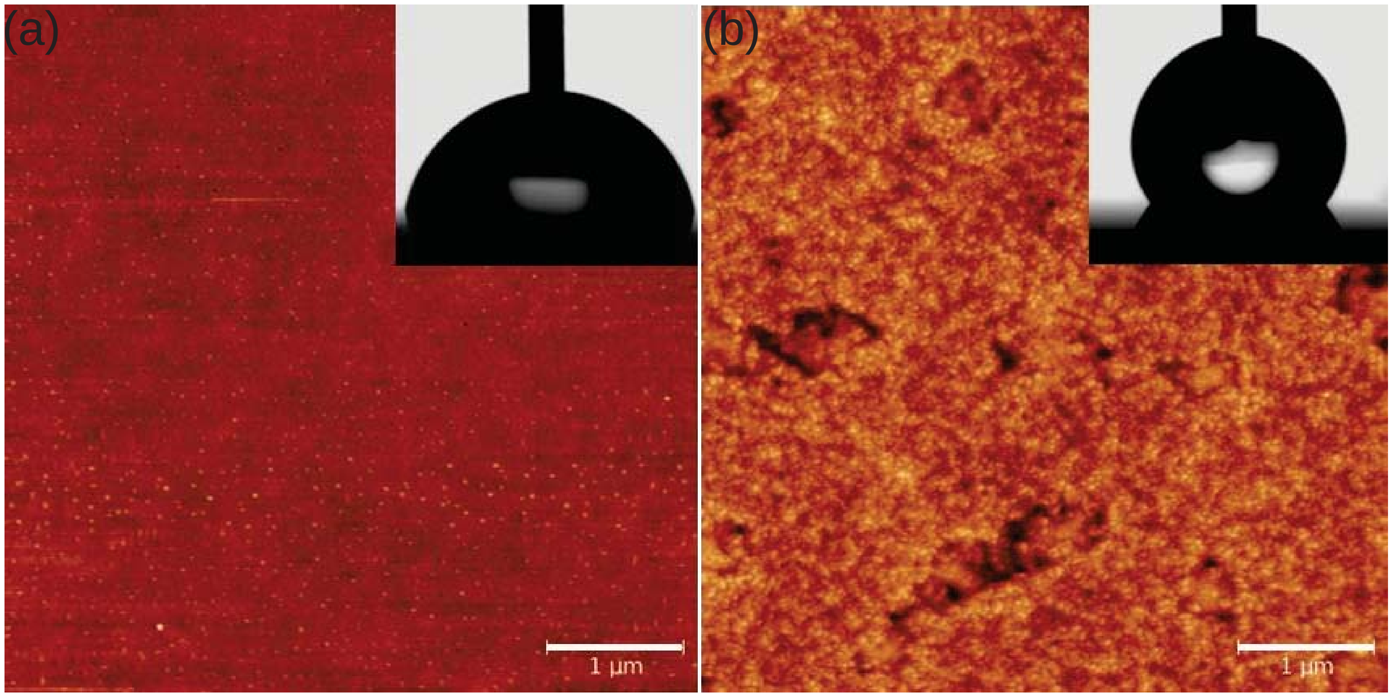
RAFT copolymerization of P(F-POSS-MA)-co-PMMA

10% F-POSS	M_n		Conv
Time (hr)	(g/mol)	PDI	%.
1*	4100	2.2	8
2	4,700	1.2	16
4	11,300	1.04	28
8	26,600	1.03	51



- **Determining impact of F-POSS on polymerization conditions**
  - No homopolymerization possible
  - Cannot polymerize well above 50 wt % F-POSS-MMA loading
  - Controlled at beginning of RAFT polymerization
  - *NMR M_n value

AFM of P(F-POSS-MA)-co-PMMA



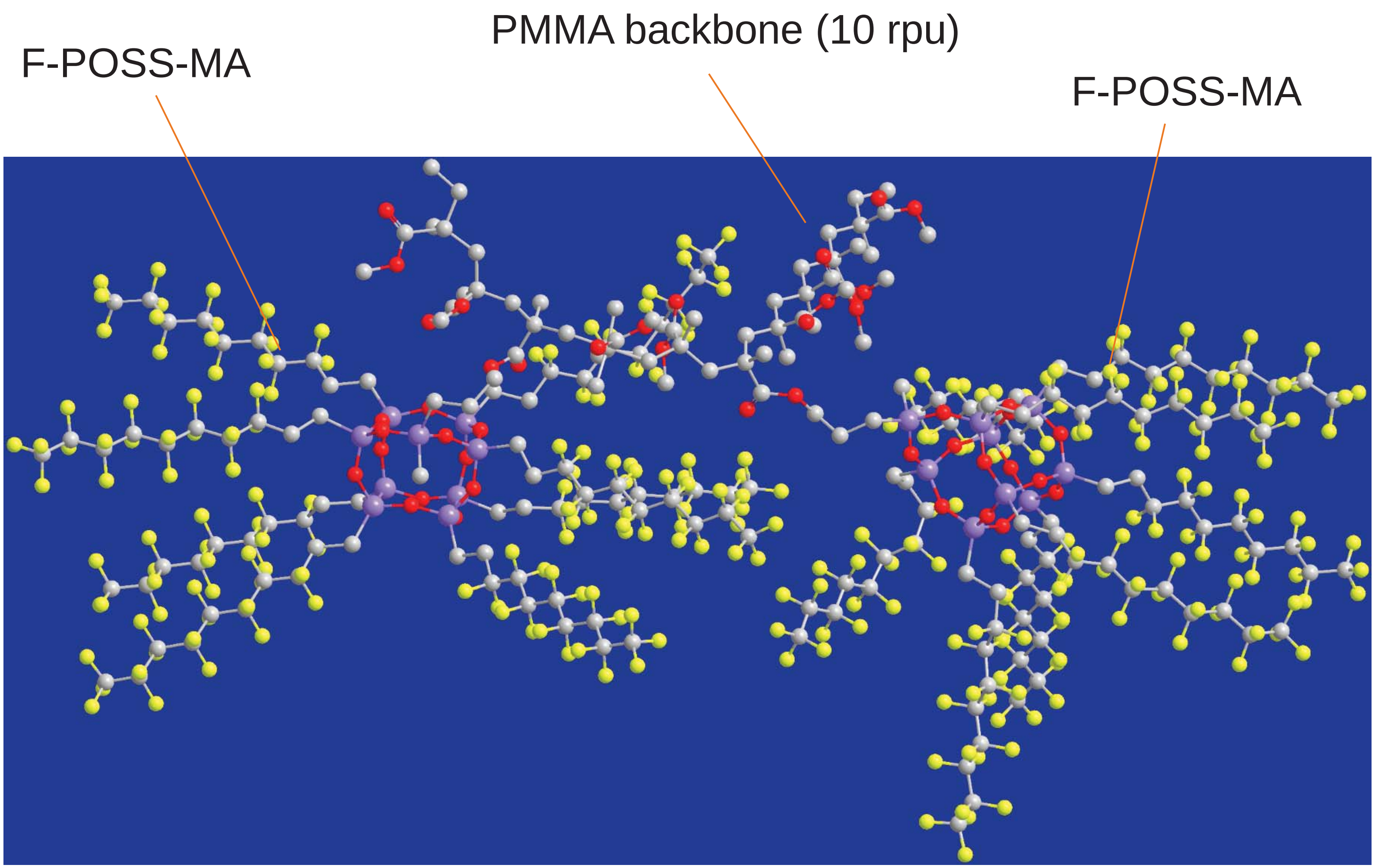
AFM images of spun cast films of copolymers on SiO_2. Corner images are pictures of static contact angle measurements with hexadecane drops. a) 1 wt.% F-POSS copolymer b) 25 wt. % F-POSS copolymer. Z scale 0 – 15 nm

AFM: Chris Sahagan

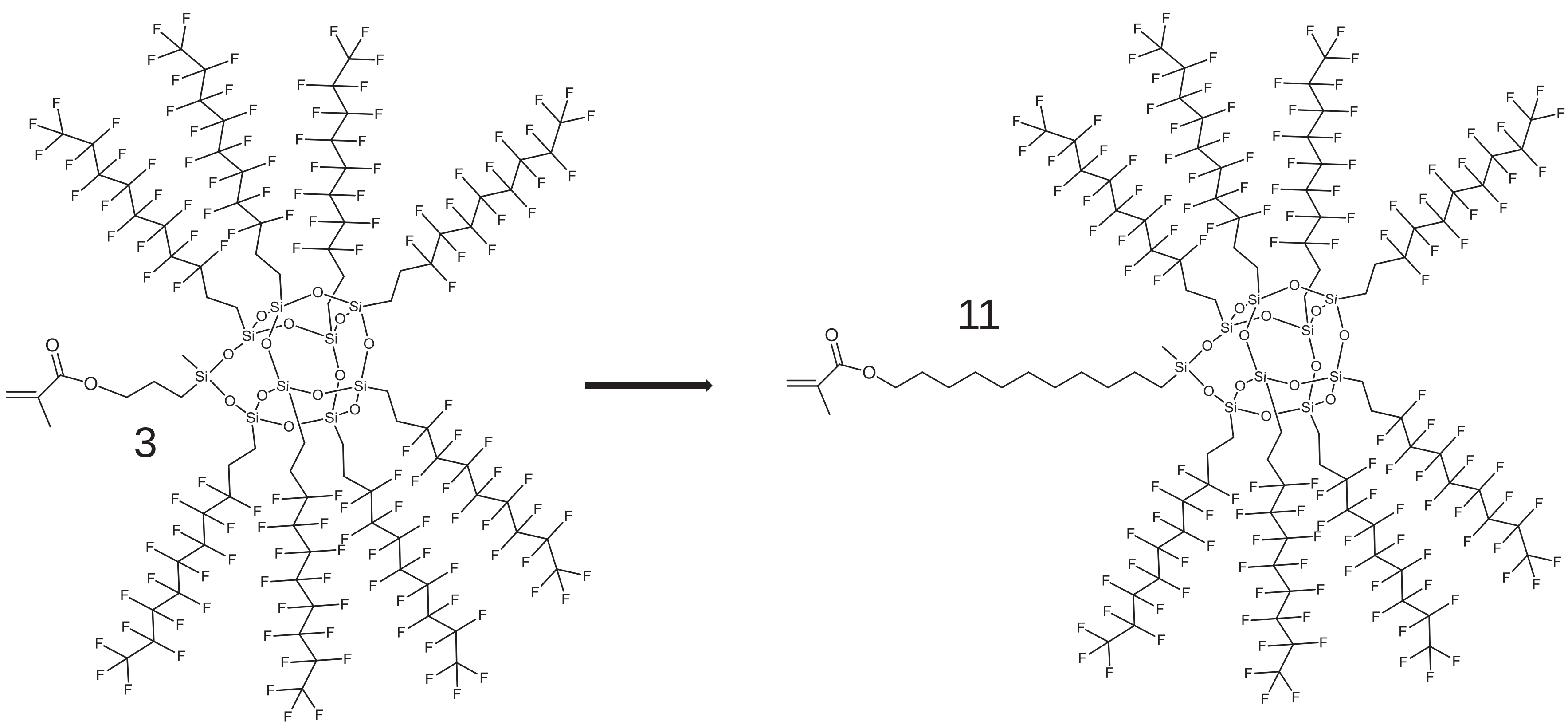
Copolymerization Summary

- Copolymerizations produced F-POSS based copolymers.
- Polymerization have trouble at higher F-POSS monomer feed ratios and are more controlled at lower conversion with RAFT initiator.
- However, we really want the homopolymer!

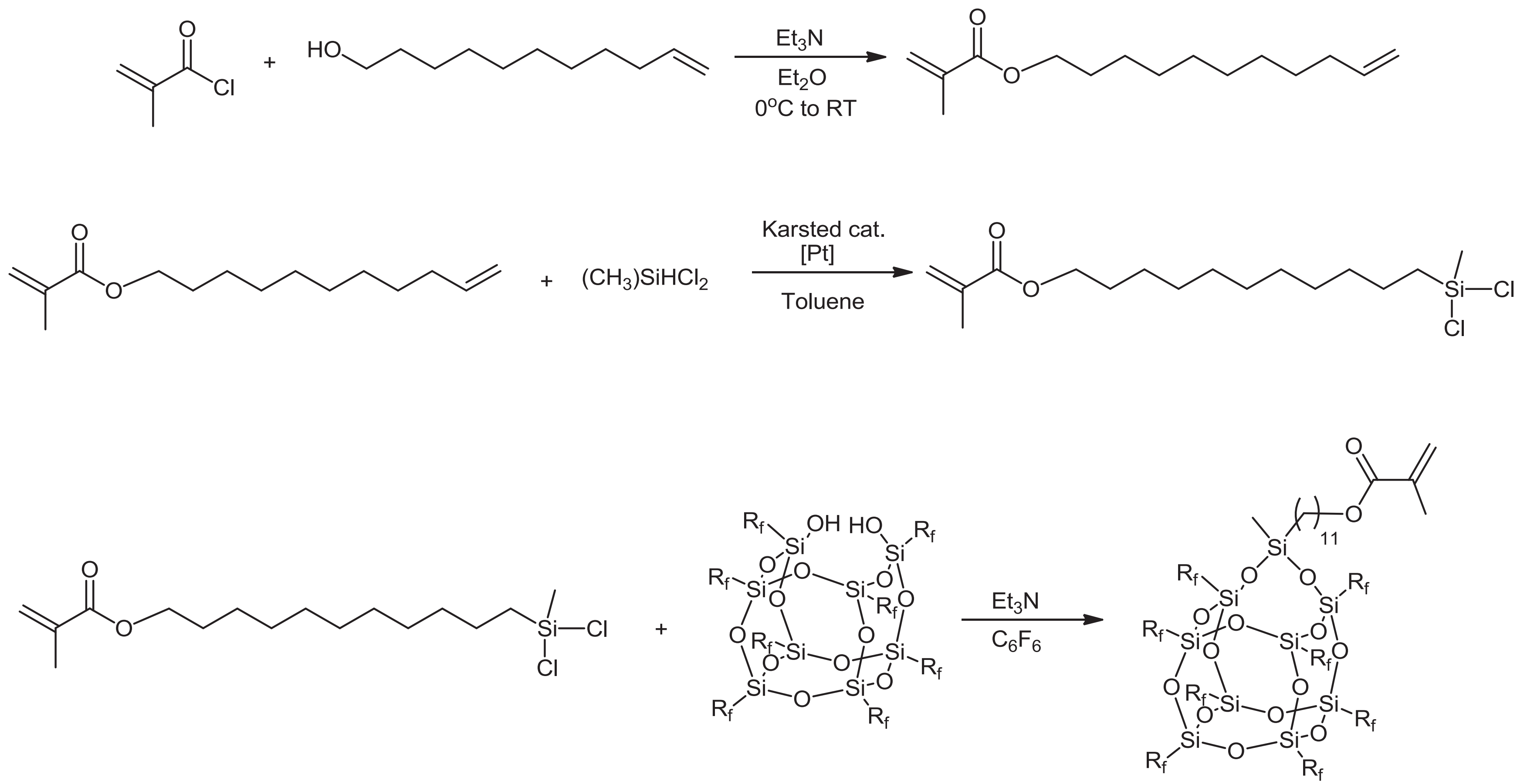
Is it crowded in here?



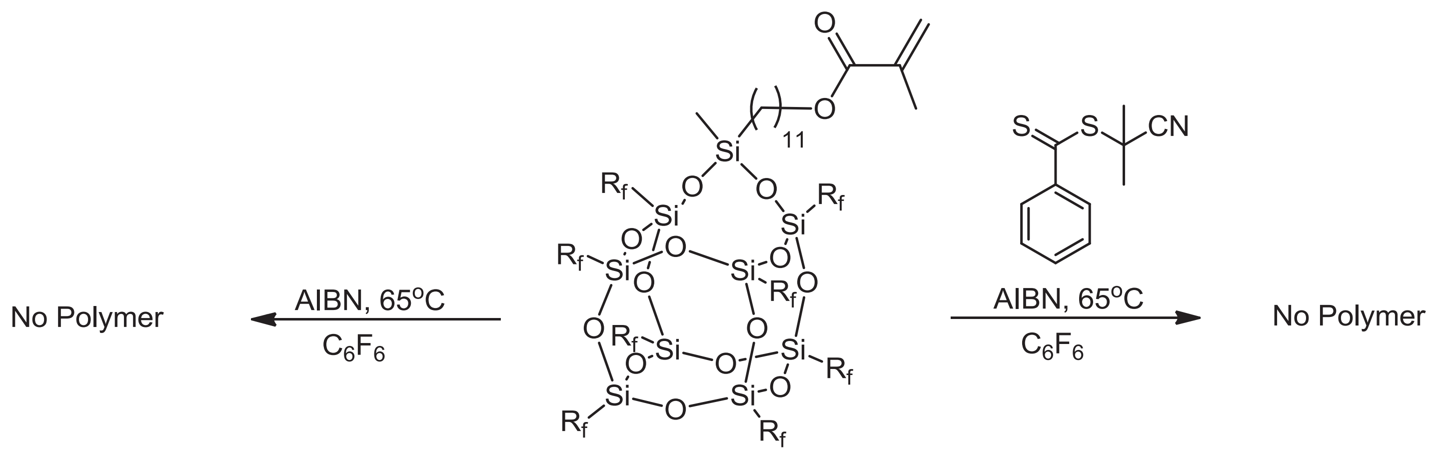
Extend the Chain



Long Chain Monomer Synthesis

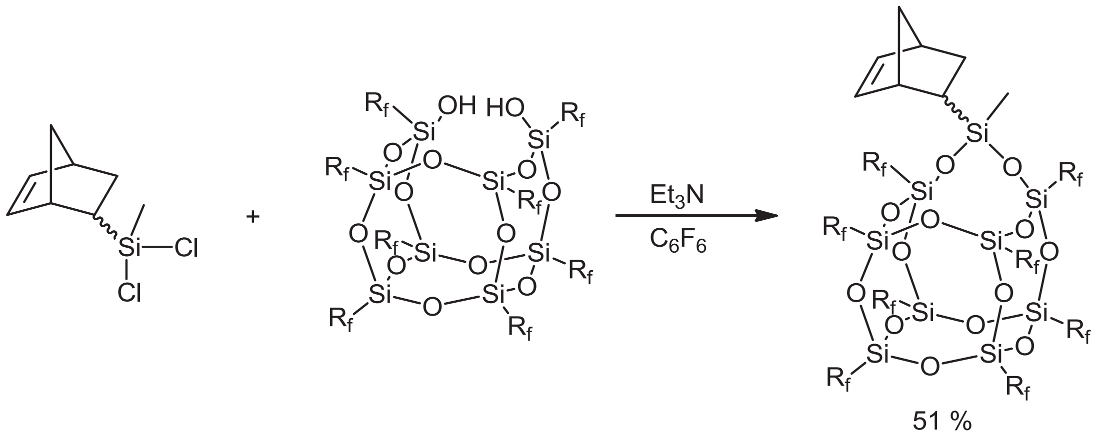


Polymerization



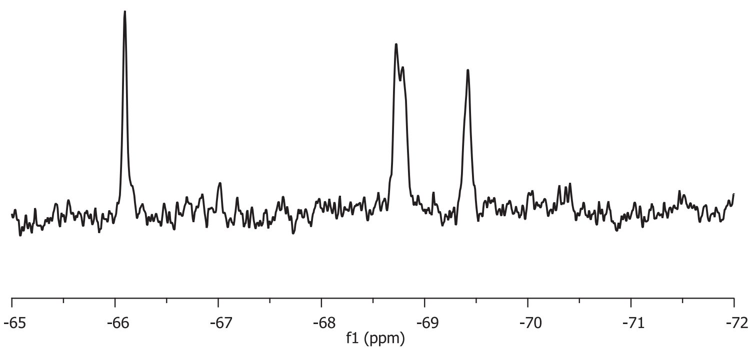
- Still no sign of free radical homopolymerization
- Copolymerizations will be attempted next

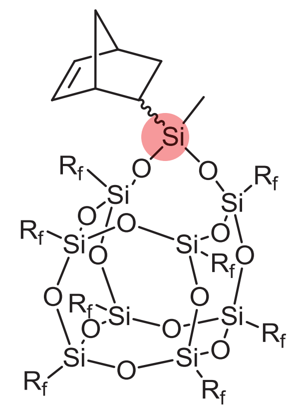
Norbornene Synthesis

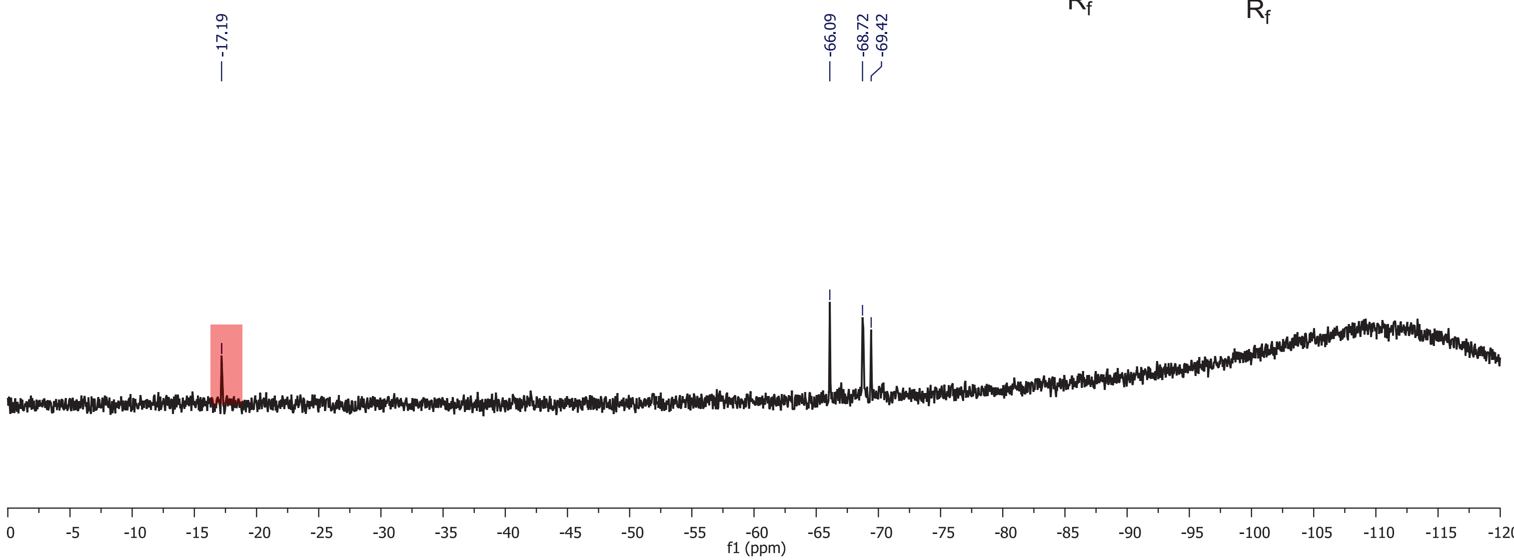


- Coupling reaction works well
  - Work-up is a bit tricky due to similar solubilities of disilanol, T8 side product, and product
  - Room for further improvement

^{29}Si NMR

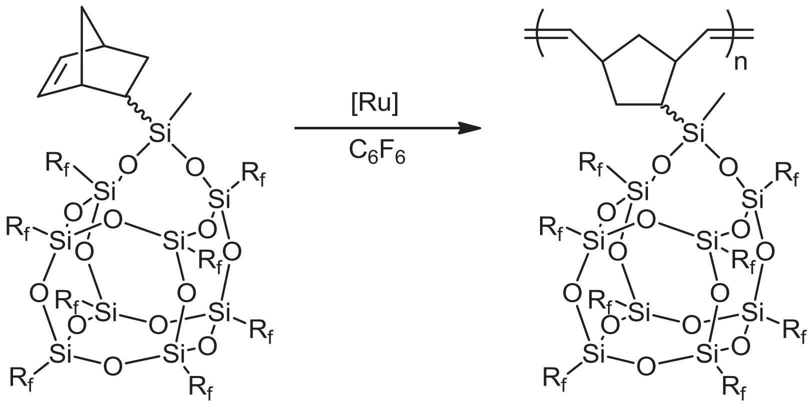




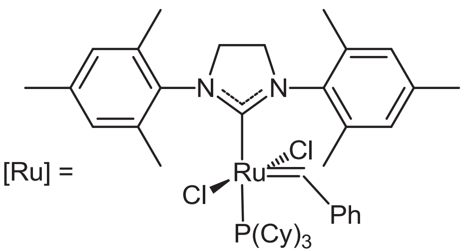


NMR: $CDCl_3/C_6F_6$

ROMP



[Ru] =



Grubb's 2nd generation catalyst (seems to be soluble in hexafluorobenzene

- Polymerization
  - Performed on 200 mg scale
  - 50:1 monomer:cat
  - Reaction of 30 minutes NMR run
  - Initial signs point to polymerization success
  - Further polymerizations will be persued

Summary

- Structures were demonstrated to be reactive towards a variety of dichlorosilanes
- Solubility of F-POSS compounds were shown to be influenced by chemical functionality
- Functionality was shown to be influential on contact angle measurements
- ROMP chemistry works well
- Currently working on other monomers and polymers for F-POSS
- F-POSS compounds have a near limitless potential in producing a variety of new hydrophobic, oleophobic, or ominiphobic polymer composites.
  - Reaction mechanisms, polymer composites, block copolymers, etc….

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pwg

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Mr. Raymond Compos*

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Mr. Kevin Lamison
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